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Abstract

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Investigation of the Structure of Surface Compounds Formed during the Adsorption of Ethanol on γ-Alumina by the Method of Infrared Absorption Spectra

The study of infrared (IR) absorption spectra of alcohols adsorbed on oxides is of considerable interest for investigating the mechanism of the reactions catalyzed by them. The aim of the present work was to study the features of the formation and structure of surface compounds arising from the interaction of ethanol with γ-Al_2O_3 at various temperatures.

Samples of γ-Al_2O_3 with a specific surface area of 270 m^2/g and a thickness of 10-15 mg/cm^2 were used in the work. The investigation was carried out on a UR-10 infrared spectrometer with a NaCl prism in the region 2000-900 cm^{-1}; a cell described in work ([1]) was used.

The absorption spectra of the surface compounds formed during the adsorption of ethanol on γ-alumina at various temperatures are shown in Fig. 1. In the absorption spectrum of γ-alumina after adsorption of ethanol at 20° and subsequent evacuation at this temperature, a series of absorption bands appears in the region 1200-1000 cm^{-1} with intense maxima at 1120, 1080, and 1060 cm^{-1} and an absorption band at 1330 cm^{-1}. Evacuation of the sample at 170° leads to the disappearance of the 1060 cm^{-1} band; the absorption bands at 1120 and 1080 cm^{-1} can be removed only by heating the adsorbent in vacuum to 350°. Adsorption of ethanol at temperatures above 170° is accompanied by the appearance in the spectra, in addition to absorption in the region 1200-1000 cm^{-1} and the maximum at 1330 cm^{-1}, of two new intense bands at 1590 and 1470 cm^{-1}, which disappear after evacuation at 400°.

Fig. 1. Schematic representation of IR spectra of surface compounds on γ-Al_2O_3. 1 —adsorption of ethanol at 20°, desorption at 20°; 2 —after desorption at 170°; 3 —adsorption at 170°, desorption at 20°; 4 —adsorption and desorption at 350°.

The absorption band at 1060 cm^{-1} can be assigned to physically adsorbed ethanol molecules bound to the oxide surface rather strongly, apparently by

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Figure 1: Fig. 1. Schematic representation of IR spectra of surface compounds on γ-Al_2O_3. 1 —adsorption of ethanol at 20°, desorption at 20°; 2 —after desorption at 170°; 3 —adsorption at 170°, desorption at 20°; 4 —adsorption and desorption at 350°

Figure 2

Figure 2: Figure 2

a hydrogen bond. In gaseous ethanol it corresponds to the band at 1080 cm^{-1}, belonging to the stretching vibration of the C—C—O bonds and the deformation vibration of OH. The remaining bands in the region 1200-1000 cm^{-1}, according to the data of Babushkin and Uvarov (2-4) and Greenler (5, 6), may be assigned to surface ethers (surface ethoxy groups) of the type $> Al - O - C_2H_5$ and are apparently due to stretching vibrations of the C—O bond in these compounds. The bands 1590 and 1470 cm^{-1}, as was shown by Greenler (5, 6), belong to a surface acetate-like compound. The frequencies of these bands coincide with the frequencies

asymmetric and symmetric valence vibrations of the group —C(=O)—O—of aluminum acetate (7). The absorption maximum at 1330 cm^{-1} is associated with the deformation vibration of the CH_3 group of the surface compounds.

Fig. 2. Absorption spectra of ethanol adsorbed at 20°, after evacuation at 170°:
1 —on γ-Al_2O_3; 2 —on γ-Al_2O_3 hydrated with H_2O^{18}

To elucidate the mechanism of formation of surface ethers on γ-Al_2O_3, we investigated the IR spectra of ethanol adsorbed on samples preliminarily hydrated with water containing 70% H_2O^{18}. The γ-Al_2O_3 samples were heated in vacuum at 400°, kept in saturated water vapor at 170°, and then evacuated at this temperature. The absorption spectrum of ethanol adsorbed on γ-Al_2O_3 treated in this way is compared in Fig. 2 with the spectrum of ethanol adsorbed under the same conditions on the initial γ-alumina. As can be seen from the figure, in the spectrum of γ-Al_2O_3 hydrated with H_2O^{18}, along with the bands at 1120 and 1080 cm^{-1}, absorption bands are observed that are shifted relative to these bands by 15 and 20 cm^{-1}, respectively, toward lower frequencies. The appearance of new bands in the spectrum is evidently due to the formation of surface ethers containing O^{18}. This permits the assertion that surface compounds of this type arise as a result of the interaction of ethanol molecules with hydroxyls of the oxide, leading to cleavage of the hydroxyl group of the alcohol and of the proton of the surface OH groups.

Figure 3

Figure 3: Figure 3

The appearance in the region 1200—1000 cm^{-1} of two intense absorption bands is attributed by us, as in the case of TiO_2 (8), to the existence of two types of surface ethers. The presence of two types of ethers on γ-Al_2O_3 is apparently due to features of the structure of the oxide crystal lattice. According to current views, atoms of aluminum in octahedral and tetrahedral coordination are present in the structure of γ-Al_2O_3, and in a number of interstices cations are absent (9). Thus, on the hydrated surface of γ-Al_2O_3 one may expect the existence of at least two qualitatively different types of hydroxyl groups, bound to aluminum atoms in octahedral and tetrahedral coordination. It should be noted, in particular, that Peri and Hannan (10), who investigated the IR spectra of γ-Al_2O_3, found on its surface three chemically different types of hydroxyl groups. Thus, the absorption bands at 1120 and 1080 cm^{-1} may probably be assigned to surface compounds of the type $>Al—O—C_2H_5$, in which aluminum is in different coordination.

Fig. 3. Schematic representation of the spectra of surface compounds on θ-Al_2O_3 (1); on γ-Al_2O_3 treated with HCl (2); on γ-Al_2O_3 treated with NaOH (3)
(a —adsorption of ethanol at 20°, desorption at 170°; b —adsorption at 300°, desorption at 170°)

This is confirmed by the data we obtained on the spectra of ethanol,

adsorbed on θ-Al_2O_3, in which the aluminum atoms are found only in octahedral coordination (^{11}), and on γ-Al_2O_3 preliminarily treated with hydrochloric acid, which, it may be assumed, blocks surface groups containing an aluminum atom in a tetrahedral environment and thus bearing a positive charge $[AlO_4]^+$.* In the spectrum of ethanol adsorbed at 20° on θ-Al_2O_3 and on HCl-treated γ-Al_2O_3 (Fig. 3), after evacuation at 170°, in the 1200-1000 cm^{-1} region only one absorption band is observed, at 1090 and 1080 cm^{-1}, respectively. On the basis of these data it may be assumed that the band at 1080 cm^{-1} in the spectrum of ethanol chemisorbed on γ-Al_2O_3 belongs to a surface ether formed with the participation of an aluminum atom in octahedral coordination, while the 1120 cm^{-1} band belongs to a surface ether with the participation of aluminum in tetrahedral coordination.

On γ-Al_2O_3 samples treated with NaOH (Fig. 3), both types of surface ethers are observed.

Fig. 4. Absorption spectra of ethanol adsorbed on γ-Al_2O_3 at 20° (1), on γ-Al_2O_3 at 200° (2), and on γ-Al_2O_3 containing O^{18} in the lattice at 200° (3), after evacuation at 20°.

To clarify the nature of the active sites on the surface of aluminum oxide

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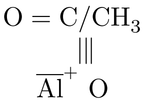
Figure 4: Fig. 4. Absorption spectra of ethanol adsorbed on γ-Al_2O_3 at 20° (1), on γ-Al_2O_3 at 200° (2), and on γ-Al_2O_3 containing O^{18} in the lattice at 200° (3), after evacuation at 20°.

at which, during adsorption of ethanol at elevated temperature, formation of an acetate-like compound occurs, samples of γ-aluminum oxide were prepared which contained, in the oxide lattice, along with O^{16} atoms also O^{18} atoms. The samples were prepared by the amalgam method ([12]) using water containing 70% H_2O^{18}. The second starting substance was chemically pure aluminum of grade AV-000. Mercury was used in the form of a nitrate salt in an amount of 0.01% of the weight of water.

The absorption spectrum of ethanol on γ-Al_2O_3 samples containing O^{18} in the crystal lattice and previously trained in vacuum at 400°, in the 1200-1000 cm^{-1} region, coincides with the spectrum of ethanol adsorbed on ordinary γ-Al_2O_3. This indicates that the formation of surface ethers occurs without participation of the oxygen of the oxide lattice. The absorption spectra of ethanol adsorbed at 350°, in the 1600-1400 cm^{-1} region (Fig. 4), however, reveal a substantial difference. In the spectrum of the acetate-like compound on γ-Al_2O_3 containing O^{18}, in addition to the bands at 1590 and 1470 cm^{-1}, additional absorption maxima are observed at 1570 and 1455 cm^{-1}. Splitting of the bands indicates the formation of a surface compound, one of whose structural elements is lattice oxygen. The structure of this compound may be represented as follows:



$$\begin{array}{c} O = C/CH_3 \\ ||| \\ \overline{\text{Al}}^{+}\ \ O \end{array}$$

Adsorption of ethanol on θ-Al_2O_3 (Fig. 3) at 300° leads to the appearance of absorption bands at 1575 and 1460 cm^{-1}, which are close to the bands of the acetate-like surface compound on γ-Al_2O_3. On HCl-treated γ-Al_2O_3, as well as on samples treated with NaOH (Fig. 3) (at a content alkali of at least 0.4 meq/g, absorption bands in the region 1600-1400 cm^{-1} are not observed. It is interesting to note that treatment of γ-Al_2O_3 with

* If it is assumed that a molecule of hydrochloric acid blocks one $[AlO_4]^+$ site, and if one proceeds from the value of the oxide surface and the fraction of the surface occupied by $[AlO_4]^+$ groups, then in order to block all such groups about two meq/g HCl is required. Taking into account that part of the acid is lost during drying and calcination of the samples, we used a one-and-a-half-fold excess of hydrochloric acid.

alkali lowers the yield of ethylene in the ethanol decomposition reaction, without substantially affecting the amount of ether formed (13). This suggests that the catalytic dehydration of ethanol to ethylene and the formation of the surface acetate-like compound are related to one another.

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